able column packings to separate the peaks from IV and VI.

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Synthesis of Methylthiomethyl Isothiocyanate

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Considerable interest has been shown in methylthioalkyl isothiocyanates of the composition $CH_3S(CH_2)_nNCS$. These mustard oils contribute to the characteristic aroma of various *Cruciferae* species.[2] A number of these compounds ($n = 2$ to 9) were synthesized by Kjaer and Christensen,[2] but the first member of this series, methylthiomethyl isothiocyanate, has not been prepared. Recently, Bailey, *et al.*,[3] using gas chromatography and mass spectrometry for isolation and identification, have suggested that this isothiocyanate is an aroma component of fresh cabbage (*Brassica oleracea* var. *capitata alba*).

The synthesis of methylthiomethyl isothiocyanate was accomplished in good yields by refluxing chloromethyl methyl sulfide and potassium thiocyanate in petroleum ether, analogously to the preparation of methoxymethyl isothiocyanate.[4,5] The new mustard oil, which has a pleasing, pungent aroma, was characterized by conversion to the thiourea and isothiuronium picrate.[6]

Chloromethyl methyl sulfide was also found to react readily with thiourea to give the isothiuronium salt.

EXPERIMENTAL[7]

Chloromethyl methyl sulfide was prepared from dimethyl sulfide and sulfur chloride by the method of Richtzenhain and Alfredsson.[8]

Methylthiomethyl isothiocyanate. A mixture of 11.5 g. (0.12 mole) of dry, powdered potassium thiocyanate, 10 g. (0.10 mole) of chloromethyl methyl sulfide, and 40 ml. of petroleum ether (b.p. 35–75°) was stirred and refluxed for 6 hr. An additional 11 g. (0.11 mole) of powdered potassium thiocyanate was added during this period. After cooling overnight at 0–5°, the yellow oil that had separated as a lower layer was dissolved by adding methylene chloride. The solid present was filtered off, and the solvent was removed from the filtrate under reduced pressure. Distillation of the concentrate at 18 mm. yielded 9.88 g. (80%) of a light yellow liquid, b.p. 83–86°. Redistillation gave a mildly pungent, colorless liquid; b.p. 82–84° (17 mm.), n_D^{19} 1.5884.

Anal. Calcd. for $C_3H_5NS_2$: C, 30.23; H, 4.23; S, 53.79. Found: C, 30.40; H, 4.27; S, 54.16.

The infrared spectrum showed the typical strong isothiocyanate band at 4.97 μ.

N-(Methylthiomethyl)thiourea. A solution of 4 g. of methylthiomethyl isothiocyanate in 100 ml. of ammonia-saturated methanol was allowed to stand at room temperature for 16 hr. After removal of the methanol under reduced pressure, crystallization from hexane–ethyl acetate yielded 2.3 g. (50%) of white crystals, m.p. 96–101°. Several recrystallizations from hexane–ethyl acetate afforded glistening white leaflets, m.p. 102–104°. The absorption spectrum in ethanol showed a maximum at 247 mμ.

Anal. Calcd. for $C_3H_8N_2S_2$: C, 26.45; H, 5.92; N, 20.57. Found: C, 26.41; H, 5.96; N, 20.50.

S-Methyl-N-(methylthiomethyl)isothiuronium picrate was prepared by refluxing the thiourea in ethanol with a slight excess of methyl iodide and subsequent addition of ethanolic picric acid.[6] The picrate crystallized from ethanol as fine yellow leaflets, m.p. 153–155°.

Anal. Calcd. for $C_{10}H_{13}N_5O_7S_2$: C, 31.66; H, 3.45; S, 16.90. Found: C, 31.73; H, 3.56; S, 17.16.

S-(Methylthiomethyl)isothiouronium chloride. When a solution of 0.5 g. (0.0066 mole) of thiourea and 0.64 g. (0.0066 mole) of chloromethyl methyl sulfide in 17 ml. of acetone was allowed to stand at room temperature,[9] cloudiness began to appear in about 5 min. The mixture was cooled in ice after 1.5 hr. at room temperature, and the oil that had separated formed a white solid; 0.80 g. (70%), m.p. 126–129°. Two crystallizations from n-propyl alcohol gave colorless prismatic crystals, m.p. 131–133°.

Anal. Calcd. for $C_3H_9ClN_2S_2$: C, 20.86; H, 5.25; S, 37.13. Found: C, 21.10; H, 5.12; S, 37.40.

The picrate crystallized from ethanol as yellow needles, m.p. 158–160°.

Anal. Calcd. for $C_9H_{11}N_5O_7S_2$: C, 29.59; H, 3.04; S, 17.55. Found: C, 29.77; H, 3.22; S, 17.64.

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5-Sulfonamido-6-aminouracils

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As part of a study of 5-substituted 6-aminouracils[1] as diuretics, a series of 5-sulfonamido-6-

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